

EFFECTIVE POTENTIAL METHOD IN A CELLULAR
FLUID MODEL. APPLICATION TO BINARY
FLUID SYSTEMS

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A method is proposed to analyze the thermal properties of fluids and their mixtures, which is based on using the effective potential (12,6) with variable potential parameters in conjunction with the equation of state for a cellular model.

As is known, the following basic assumptions are used in cellular theory: a single particle fills the cells forming the quasicrystalline fluid structure, the energy of interaction between the molecule selected and all the rest is replaced by a self-consistent field, and there is no interaction between cells.

In this model the statistical integral Z_N can be written in the form

$$Z_N = z^N,$$

$$z = v_f \exp \left[-\frac{E(0)}{2kT} \right] \frac{h}{(2\pi mkT)^{1/2}}, \quad (1)$$

$$v_f = \int_{\Delta} \exp \left[-\frac{E(\vec{r}) - E(0)}{kT} \right] d\vec{r}. \quad (2)$$

The main difficulty in using (1) to obtain the equation of state is the evaluation of the "free volume" v_f . The integration in (2) is performed with respect to the whole cell volume, and in principle it can be performed if the molecule energy $E(\vec{r})$ is known. One of the methods to determine $E(\vec{r})$, proposed by Frenkel [2], is to replace $E(\vec{r})$ by a certain mean value $\chi(v)$ determined from the condition

$$\int_{\Delta} \exp \left[-\frac{E(\vec{r})}{kT} \right] d\vec{r} = v \exp \left[-\frac{\chi(v)}{kT} \right],$$

where $\chi(v)$ is a function of the cell volume v ($v = V/N$).

Let us note that this assumption is sufficiently rigorous if the configuration of the potential field within the cell [2] is taken into account for densities corresponding to the fluid density.

The function $\chi(v)$ for the Lennard-Jones potential (m, n) has the form

$$\chi(v) = -\frac{c}{v^\mu} + \frac{d}{v^\nu} \quad \left(\mu = \frac{n}{3}, \quad \nu = \frac{m}{3} \right),$$

which, in conformity with [2], results in the equation of state

$$p = \frac{kT}{v} - \frac{c\mu}{v^{\mu+1}} + \frac{d\nu}{v^{\nu+1}}. \quad (3)$$

For the potential (12,6) $\mu = 2$, $\nu = 4$ and the equation becomes

$$p = \frac{NkT}{v} - \frac{\alpha}{v^3} + \frac{\beta}{v^5} \quad (\alpha = 2cN^3, \quad \beta = 4dN^5), \quad (4)$$

$$\alpha \sim \varepsilon\sigma^6, \quad \beta \sim \varepsilon\sigma^{12}. \quad (5)$$

Since α and β are constants, then (4) is not suitable for a correct description of the temperature dependence of the fluid properties, while the density dependence is theoretically founded. To eliminate the mentioned

disadvantage, it should evidently be assumed that α and β are functions of the temperature. This can be achieved in a natural way if the effective potential with temperature-dependent parameters ε and σ are used in (5).

To eliminate the structure of the proportionality factors in (5), let us write the relationship

$$\sqrt{\frac{\beta}{\alpha}} = \frac{N\sqrt{2}}{\gamma} \sigma^3, \quad \frac{\alpha^2}{\beta} = 4\bar{z}N\varepsilon, \quad (6)$$

where \bar{z} is the coordination number and γ is a structural factor characterizing the cell geometry and its associated volume v , and the spacings between the nearest neighbors a are related by $\gamma v = a^3$.

It is easy to obtain (6) if a cell is considered in which $a = R_e$. In fact, in this case the cell volume and energy E equal, respectively, $v = R_e^3/\gamma = \sqrt{2}\sigma^3/\gamma$ and $E = \bar{z}\varepsilon$, but for one mole of fluid $v = N\sqrt{2}\sigma^3/\gamma$ and $E_N = \bar{z}N\varepsilon$. Since the interaction forces between molecules are zero for $a = R_e$, the fluid system under consideration then consists of noninteracting particles, and its volume is the ideal-gas volume of the fluid ($v = V_{id} = RT/p$). On the other hand, $V_{id} = \sqrt{\beta/\alpha}$ on the basis of (4), and we arrive at the first of relationships (6). Now, if the energy of the whole system is calculated, then it will equal $N\chi(v) = 1/4\alpha^2/\beta$. (It is here taken into account that the mean value of the molecule energy corresponds to its position at the cell center in the case under consideration.) We therefore obtain $1/4\alpha^2/\beta = N\bar{z}\varepsilon$, i.e., the second relationship in (6). It is easy to see that the proportionality factors in (6), and therefore in (5) as well, are universal quantities. In fact, $\gamma = idem$ and $\bar{z} = idem$ for the lattice type selected (e.g., $\gamma = \sqrt{2}$ and $\bar{z} = 12$ for a fcc lattice). Hence, without yielding preference to any type of lattice, it can be considered that the proportionality factors in (5) are common to all substances.

An analysis of (6) shows that the dependence of α and β on the temperature is due to the following factors.

1. The inadequacy of the actual pairwise intramolecular potential to the Lennard-Jones potential (12, 6) (even for such a simple substance as Ar [3]). As has been shown earlier in investigations of the properties of gases [4-7], this results in a temperature dependence of the model potential parameters ε and σ .

2. Structural changes taking place in the fluid with the change in temperature, and consequently, to the temperature dependence of \bar{z} and γ . For instance, as the temperature changes from 84.9 to 124.2°K for Ar the \bar{z} varies between 12.2 [8] and 6.1 [9], and according to the data in [10], between 12.7 and 11.5.

Therefore, the quantities in the left-hand side of (6) and, therefore, the coefficients of (4) are functions of the temperature. Desiring to conserve the universal nature of the proportionality factors in (5) and taking account of the difficulties in determining the temperature dependences of \bar{z} and γ , we consider them constant, and we hence obtain

$$\sqrt{\frac{\beta(T)}{\alpha(T)}} = M\sigma^3(T), \quad \frac{\alpha^2(T)}{\beta(T)} = L \frac{(\varepsilon T)}{k}, \quad (7)$$

where M and L are common constants for all the substances.

Therefore, it is assumed in conformity with (7) that not only the intensity of the intramolecular interaction but also the change in fluid structure will be determined by the temperature dependence of ε and σ .

Literature data for the parameters ε and σ of the Lennard-Jones potential (12, 6) and test pvT data for different fluids can be used to determine the values of the universal constants M and L . For instance, taking the standard values $\sigma = 3.405 \text{ \AA}$ and $\varepsilon/k = 119.8^\circ\text{K}$ for Ar and using the pvT data on the critical isotherm to find α and β by means of (4), we obtain

$$M = 0.8606, \quad L = 31.1562. \quad (8)$$

Calculations of the constants M and L on the basis of data for Ne, Kr, Xe, and CH_4 result in quite similar results. Hence, as before, the most confident values of the potential parameters and the pvT data on the critical isotherm of the substances mentioned have been used. The selection of the critical isotherm is preferable as compared to others since it is a natural boundary for the domain of existence of the fluid.

Thus, by using (8), (7), (5), and (4), we finally arrive at the equation of state

$$\frac{pv}{NkT} = 1 - 1.744 \frac{\varepsilon}{kT} \left[\left(\frac{b_0}{V} \right)^2 - 0.4654 \left(\frac{b_0}{v} \right)^4 \right]. \quad (9)$$

Let us note that the specific temperature dependence of ϵ and σ is determined from the condition of best compliance with the pVT test data for the fluid under investigation (by a comparatively simple method which we do not examine here).

The principle of the universality of an effective potential affords the possibility of using (9) for any fluids, starting from simple and ending with complex polars.

We verified the suitability of the equation of state (9) with temperature-dependent ϵ and σ to describe the pVT properties of pure fluids in extensive experimental material. The verification, performed on such fluids as Ar, Kr, N₂, O₂, CH₄, C₂H₆, H₂O, CH₄O, C₂H₆O, etc., showed that in complete conformity with the accepted physical model the equation of state (9) with $\sigma(T)$ and $\epsilon(T)$ determined from pVT test data describes the thermal properties of all the systems listed above with a 0.1-0.2% error in the density in the temperature range $T_{tr} < T < T_{cr}$ and density range of $1.8\rho_{cr}$ and higher (e.g., for H₂O $\delta\rho_{av} \approx 0.05\%$, $\delta\rho_{max} = 0.15\%$).

Analysis of the results of the comparison on many substances permits the assertion that (9) does not yield to the best precision equations of state and can be recommended for the computation of the thermodynamic properties of fluids. However, in comparison with empirical equations of state it has the advantage that it has a theoretical basis and the parameters of this equation have a specific physical meaning.

In this connection, we recommend it for the investigation of fluid mixtures and the prediction of their properties according to the data of the pure components. For this purpose it is convenient to use the results of the theory of conformal solutions since the form of the dual potential is taken identical for all fluids and agrees with the Lennard-Jones (12, 6) potential at a fixed temperature. As has been shown in [11], within the framework of the theory of conformal solutions, the single-fluid approximation is best which establishes the following relation between the potential parameters of the pure fluids and the solution they form in a general way:

$$f(\epsilon, \sigma) = \sum_i \sum_j f(\epsilon_{ij}, \sigma_{ij}) x_i x_j. \quad (10)$$

Here f is some function of the potential parameters whose specific form is determined by the model taken for the solution. It is easy to see that the known Vander Waals combination rules are a particular case of (10). In our case two sets of combination rules are best (this was established from extensive experimental material):

$$\epsilon\sigma^3 = \sum_i \sum_j \epsilon_{ij} \sigma_{ij}^3 x_i x_j, \quad \sigma^3 = \sum_i \sum_j \sigma_{ij}^3 x_i x_j, \quad (11)$$

$$\epsilon\sigma^3 = \sum_i \sum_j \epsilon_{ij} \sigma_{ij}^3 x_i x_j, \quad \epsilon = \sum_i \sum_j \epsilon_{ij} x_i x_j, \quad (12)$$

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}, \quad \sigma_{ij} = 1/2(\sigma_{ii} + \sigma_{jj}),$$

which permit the prediction of a dependence of the thermal properties of a binary fluid system on the temperature, pressure, and composition with a mean error of 0.5-0.7% in the density and $\delta\rho_{max} = 1.5\%$. Such complex systems as methyl alcohol-water and ethyl alcohol-water were moreover described with such a maximal error. The maximum error was lower for systems consisting of molecules with low or zero dipole moment, and did not reach 1% in the majority of cases.

The combination rules (11) and (12) were tested in such mixtures as Ar-Kr, Ar-CH₄, O₂-N₂, Ar-O₂, CH₄-CF₄, CF₄-C₃H₆, C₂H₆-C₃H₆, CH₄-C₃H₆, H₂O-CH₄O, H₂O-C₂H₆O which contain components of different molecular complexity, where the volume effects of the mixing were described correctly.

Results of comparing the computed and test data on the mixing volumes and densities of certain fluid mixtures, which confirm the reliability of the method proposed, are represented selectively in Figs. 1 and 2 and Table 1.

Let us mention that (11) must be used for mixtures with a negative mixing volume, and (12) for mixtures with a positive volume. We have proposed a criterion by which the combination rules (11) or (12) should be selected for any fluid mixture, which results from the following considerations.

On the basis of (9), the so-called zero volume v_0 corresponding to the pressure $p = 0$ (for a fixed temperature T) can be calculated easily. By determining it for the component fluids (v_{0i}) and for the solution of given composition (v_0) [taking (11) and (12) into account], the excess volume at zero pressure can be calculated without difficulty and its sign can be determined ($v_0^E = v_0 - \sum v_{0i} x_i$). It is established that $v_0^E \leq 0$ for (11) always, while either $v_0^E \leq 0$ or $v_0^E > 0$ can hold for (12).

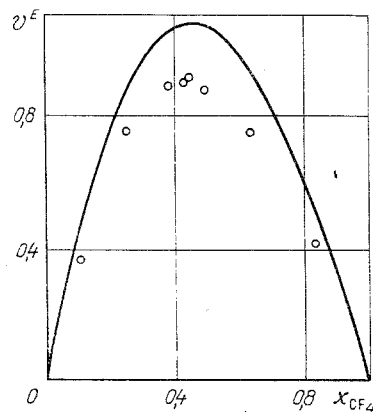


Fig. 1

Fig. 1. Mixing volume v , cm^3/mole , of system $\text{CH}_4 - \text{CF}_4$ at $T = 106.7^\circ\text{K}$; points are the test data [15] and the curve is the computation.

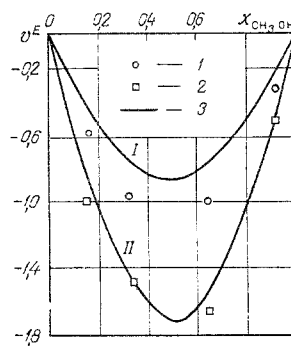


Fig. 2

Fig. 2. Mixing volume of $\text{H}_2\text{O} - \text{CH}_3\text{OH}$ for T , $^\circ\text{K}$: I) 323.15; II) 423.15; 1, 2) test data [13]; 3) computation.

The recommended criterion is characterized by the fact that we evaluate v_0^E for a given temperature T by using (12). If $v_0^E < 0$ here, then the combination rule (11) should be used as being most exact. If $v_0^E > 0$, then (12) should be used [both relationships (11) and (12) yield identical results for $v_0^E \approx 0$].

Discussion of the Results

Despite the fact that the dependence of the parameters ε and σ on the temperature is conditional, it can yield a certain representation about the change in fluid structure and in the nature of the intramolecular interaction.

Curves of ε and σ are presented in Fig. 3a for Ar found from p_vT test data. It is seen that the parameter ε grows abruptly as the temperature diminishes, becoming more than double on approaching the triple point. According to the model being used, such a history of $\varepsilon(T)$ should indicate not only a more intense intramolecular interaction, but also a magnitude of the coordination number characterizing the nearest neighborhood of the molecules which (the number \bar{z}) increases with the reduction in temperature. Moreover, from the relationship $F = -(dU_{L-J}/dr)_{r=\sigma} = 24\varepsilon/\sigma$ and the nature of the change in ε and σ it is seen that the interaction force F increases abruptly with the diminution in the temperature, which indicates the predominating effect of the repulsion between molecules in the fluid as the triple point is approached (the melting point). This agrees with the principal assumption of the lattice model, that each molecule is maintained within a small volume by repulsive forces from their neighbors. Such an assumption becomes all the more valid with the approach to the fluid triple point.

The graph presented is typical for ordinary fluids. However, the anomalous behavior of the dependence $\varepsilon(T)$ (Fig. 3b) is observed for water. As the temperature rises from 0° , growth of the parameter ε is observed. This should result in growth of the coordination number \bar{z} and, in the long run, of the fluid density. One of the factors specifying such a behavior is apparently the anomalous dependence of the water density on the temperature near 4°C .

Let us note an interesting peculiarity of the equation of state (9). The relationship

$$V_{id} = 0.6822 b_0 \quad (13)$$

TABLE 1. Comparison of Computed and Test Data [12] of the Molar Volume v (cm^3/mole) of the System Ar - Kr for $x_{\text{Ar}} = 0.491$

$T=119.98^\circ\text{K}$				$T=141.58^\circ\text{K}$			
p_{atm}	v_{test}	v_{comp}	$\delta, \%$	p_{atm}	v_{test}	v_{comp}	$\delta, \%$
9.4	33.91	33.97	0.18	30.5	37.58	37.42	-0.42
98.8	33.14	33.24	0.30	100.4	36.35	36.33	-0.08
198.3	32.45	32.55	0.31	199.6	35.10	35.18	0.23
457.4	31.13	31.23	0.32	298.9	34.18	34.23	0.15

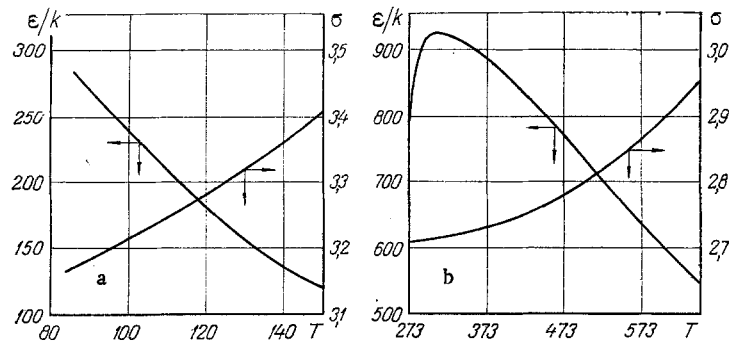


Fig. 3. Dependence of the parameters ϵ/k , $^{\circ}\text{K}$, and σ , \AA on the temperature: a) for Ar, found from tabulated data [16]; b) for water, found from tabulated data [17].

resulting from (9) should be satisfied at all points of the ideal gas curve corresponding to the fluid domain (for which $p = RT/v$).

Hence, the parameter b_0 (or σ^3) can be given a macroscopic (thermodynamic) meaning by interpreting it as a quantity proportional to the ideal-gas volume of the fluid. It is known that the density ρ_{id} along the ideal gas curve is a function of just the temperature (one parameter). This can be an additional foundation for the introduction of a temperature dependence for the parameter σ . Let us note that the fluid density ρ_{id} , evaluated for all the substances we investigated in conformity with (13), will reproduce the ideal gas curve $\rho_{id} = \rho(T)$, found by means of (tabulated) thermal test data for different substances [14], with an error of $\delta\rho = 0.1-0.3\%$. This result indicates the correct temperature history of the parameter σ .

In connection with the above, it is pertinent to touch upon the question of the possible dependence of the parameters σ and ϵ on the density. Within the framework of the model used, when the assumption about the dual nature of the multiparticle interaction is basic, such a possibility is excluded. This is explained by the fact that in going over to the equation of state in conformity with the formula $p = kT(\partial \ln Z_N / \partial v)_T$, the parameters σ and ϵ are not differentiated with respect to v . Hence, they can depend only on T for pure fluids, or on (T, x) for mixtures, but not on the state parameter v .

At the same time, we arrive at unique results if we evaluate the internal energy, entropy, and other caloric functions [by the statistical sum method or on the basis of the equation of state (9)], hence allowing differentiation of the parameters σ and ϵ with respect to temperature.

The above elucidation is for any theory in which an assumption is made about the dual additivity of the multiparticle interaction energy. If this assumption is not made, then the effective potential of the multiparticle interaction can depend on both the temperature and the density.

NOTATION

p , pressure, MPa; v , T , volume and temperature; T_{tr} , triple-point temperature; T_{cr} , critical temperature; U_{L-J} , Lennard-Jones potential (12,6) ϵ , σ , R_e , potential parameters; $b_0 = (2/3)\pi N\sigma^3$; N , Avogadro's number; m , molecule mass; h , Planck's constant; k , Boltzmann constant; r , distance from the center of the cell; x_i , molar fraction of the i -th component.

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INVESTIGATION OF THERMAL CONDUCTIVITY OF LIQUID FORMATES AT HIGH TEMPERATURES AND PRESSURES

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Experimental data on the thermal conductivity of butyl formate and octyl formate in a wide range of temperatures and pressures are given.

The experimental investigation of the thermal conductivity of liquids at high temperatures and pressures involves considerable technical difficulties. The conduction of investigations at high pressures and high temperatures necessitates the design of special and complex apparatus.

The data in [1] mainly characterize the temperature dependence of the thermal conductivity of formates at atmospheric pressure. It is only in recent time that investigations of the thermal conductivity of formates in relation to temperature and pressure have been undertaken. In [2], e.g., the results of measurement of the thermal conductivity of formates in relation to temperature at relatively low pressures (1-49 MPa) are given.

In the present paper, which represents the continuation of previous research [3-9], we give the results of an experimental investigation of the thermal conductivity of butyl and octyl formates at temperatures from room to 620°K and pressures up to 147 MPa. The measurements were made by the steady heating method on a newly designed version of a cylindrical bicalorimeter.

The theory of the method and the measurement procedure are described in detail in [6, 9].

The bicalorimeter consists of two coaxial cylinders. The gap between the cylinders is filled with the liquid under investigation. The inner cylinder (core) is made of M1 copper. The working surfaces of the core are thoroughly ground, chrome-plated, and polished. The outer cylinder is a massive copper block, into which a tube of 1Kh18N9T stainless steel is pressed. As distinct from the previous design [6], lens sealing was used to maintain the high pressure.

The main dimensions of the bicalorimeter are: inner diameter of copper block 9.99 ± 0.01 mm, diameter of copper core 9.010 ± 0.002 mm, length of measuring section 80 mm.

The experimental determination of thermal conductivity reduces to measurement of the time lag of the core temperature relative to the block temperature. For these measurements we used an R-345 potentiometer and a 51-SD timer, and for creation and measurement of the pressure we used an MP-2500 loaded-piston gauge and a set of standard gauges. In the calculation of the thermal conductivity we introduced all the corrections